



Coke-free direct formic acid solid oxide fuel cells operating at intermediate temperatures

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HIGHLIGHTS

- ▶ Formic acid is used as a fuel for solid oxide fuel cells for the first time.
- ▶ Coke formation on Ni–YSZ anode in formic acid vapor is negligible above 600 °C.
- ▶ Peak power density of 571 mW cm^{−2} is obtained with formic acid at 800 °C.

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ABSTRACT

Formic acid is investigated as a fuel for Solid Oxide Fuel Cells (SOFCs) for the first time. Thermodynamic calculations demonstrate that carbon deposition is avoidable above 600 °C. The carbon deposition properties are also investigated experimentally by first treating a nickel plus yttria-stabilized zirconia (Ni–YSZ) anode material in particle form under a formic acid-containing atmosphere for a limited time at 500–800 °C and then analyzing the particles by O₂–TPO. This analysis confirms that carbon deposition on Ni–YSZ is weak above 600 °C. We further treat half-cells composed of YSZ electrolyte and Ni–YSZ anode under formic acid-containing atmosphere at 600, 700 and 800 °C; the anodes maintain their original geometric shape and microstructure and show no obvious weight gain. It suggests that formic acid can be directly fed into SOFCs constructed with conventional nickel-based cermet anodes. *I*–*V* tests show that the cell delivers a promising peak power density of 571 mW cm^{−2} at 800 °C. In addition, the cells also show good performance stability. The results indicate that formic acid is highly promising as a direct fuel for SOFCs without the need for cell material modifications.

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1. Introduction

As highly efficient electrochemical energy conversion devices, fuel cells are known to be one of the most ideal clean power generation technologies for the future. Due to their size flexibility, fuel cells have potential applications in a wide range of fields with power outputs varying from several microwatts to megawatts. Recently, fuel cells have been seriously considered as power sources to replace lithium-ion batteries in portable electronic devices, motivated by their much higher energy density and fast “recharging” capability [1,2]. Differing from batteries, which store electric power in their electrodes, fuel cells produce electricity through the electrochemical oxidization of a fuel over the anode [3]. Thus, a suitable fuel is also critical for the realization of practical applications of fuel cells as portable power sources,

which requires high energy density, light weight and a high safety margin. Although hydrogen is an ideal fuel for fuel cells from the aspects of clean “burning” and high reactivity, the lack of a public infrastructure for hydrogen production, storage and transportation seriously hinders the widespread application of hydrogen fuel cells in the near future. In particular, the low gravimetric energy density of hydrogen discourages its use as a fuel for portable applications.

During the past 15 years, direct methanol fuel cells (DMFCs) based on polymer electrolyte membrane fuel cells (PEMFCs) have been extensively investigated as potential power sources for portable applications [4–7] due to the much higher volumetric energy density and easier storage of liquid methanol than gaseous hydrogen. However, there are several drawbacks associated with the DMFCs based on PEMFCs including the toxicity of methanol, mixed potential due to the permeability of the Nafion electrolyte membrane for methanol, likely poisoning of precious metal catalysts by intermediate reaction products with methanol and low cell voltage and power output [8–10].

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Recently, formic acid (HCOOH) has also attracted attention as a potential fuel for portable fuel cells [11–14]. As the simplest carboxylic acid existing in a liquid state at room temperature, formic acid can be produced from biomass and is widely applied as a food preservative at very low concentrations. Currently, there are two main methods for using formic acid as a fuel in fuel cells: it is either pre-reformed into hydrogen [11] or directly applied to the PEMFCs [12–14]. The direct feeding of formic acid to fuel cells is more attractive because it eliminates the need for the complicated catalytic reforming process. Unfortunately, to date, the power output of direct formic acid fuel cells using PEMFCs has seldom exceeded 100 mW cm^{-2} [12–14].

Among the various types of fuel cells, solid oxide fuel cells (SOFCs), which have all solid components and operate at elevated temperatures, have the significant advantage of fuel flexibility over low-temperature fuel cells including PEMFCs [15–18]. In principle, any combustible chemical, e.g., hydrocarbons or oxygenated hydrocarbons, can be directly applied in SOFCs to generate electric power without a pre-reforming process. However, the development of SOFCs operating on these carbon-containing fuels still faces many important challenges; for example, coke formation and poor power output are often experienced in cells with conventional nickel cermet electrodes [19–22]. Although many efforts have been made to develop alternative anode materials that are more resistant to carbon deposition with promising results [23–30], the conventional nickel plus 8 mol% yttria-stabilized zirconia (Ni–YSZ) cermets, which have been used for decades, remain the most promising anode compositions considering the inherent trade-offs among price, activity and compatibility with other cell components.

In this study, we report for the first time the direct operation of SOFCs with formic acid for efficient electric power generation. The carbon deposition of formic acid over a traditional Ni–YSZ anode was investigated. Due to the high oxygen-to-carbon ratio and lack of carbon–carbon bonds in the formic acid molecule, almost no elemental carbon was detected on the anode in operation at temperatures higher than 600°C . A promising cell power output at intermediate temperature was realized by using an SOFC with a state-of-the-art Ni–YSZ cermet anode without any modification of the cell components.

2. Experimental

2.1. Cell fabrication

The cells investigated in this study were constructed in an anode-supported thin-film electrolyte configuration, consisting of an NiO plus YSZ anode, a YSZ electrolyte, an $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) buffer layer and an $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode. The weight ratio of NiO to YSZ in the unreduced anode was fixed at 60:40. The precursor YSZ, LSCF and SDC powders were prepared by a complexing sol–gel process using both EDTA and citric acid as the complexing agents; the NiO was a commercial product of analytical grade (Chengdu Shudu Nano-science Co., Ltd.). The NiO+YSZ anode substrate with the thickness of 1.0 mm was prepared by a tape casting method, and the YSZ electrolyte was prepared by spray deposition on the anode substrate to a thickness of approximately $5 \mu\text{m}$. The anode substrate was pre-calcined at 1050°C to create sufficient mechanical strength and remove any organic matter. The as-prepared anode-electrolyte dual-layer cells were sintered at 1450°C in air to allow the densification of the electrolyte layer. An SDC buffer layer ($\sim 5 \mu\text{m}$), which was used to avoid direct contact between the cathode and YSZ electrolyte and thus the potential solid-phase side-reaction between cathode and YSZ electrolyte, was coated onto the sintered YSZ electrolyte surface by the same

spray deposition method and sintered at 1300°C in air. The LSCF cathode ($\sim 25 \mu\text{m}$) was sprayed on the top of the SDC buffer layer and fired at 1000°C for 2 h.

2.2. Electrochemical tests

Silver paste was selected as the current collector for the LSCF cathode for the I – V polarization test, which had an effective geometric surface area of approximately 0.48 cm^2 , and a mesh-like silver current collector was applied for the cell performance stability test. The fuel cell was sealed on a quartz tube (A) with an inner diameter (ID) of 10 mm using concentrated silver paste. After sealing, the cathode was directly exposed to ambient air, and the anode was fed with diluted formic acid vapor through a smaller quartz tube (B) with an outer diameter of 6 mm and an ID of 4 mm, which was penetrated into quartz tube A. The fuel gas, after reaching the anode, exited the anode chamber through the gap between quartz tubes A and B. To introduce the fuel as a gas, formic acid was vaporized by heating it to 78.8°C and carried by a nitrogen flow; the formic acid concentration in the fuel gas was approximately 50%. The fuel cell performance was tested by measuring I – V polarization curves, and the data were collected with a digital SourceMeter (Keithley 2420, USA) using a four-probe configuration.

2.3. Characterization and analysis

The thermodynamic equilibrium composition of formic acid decomposition products and the standard molar reaction enthalpies of the decomposition reactions of formic acid were analyzed using thermodynamics software (HSC Chemistry 6.0). The tendency for carbon deposition on anode was also evaluated by a post-analysis of the anode particles by oxygen temperature-programmed oxidation (O_2 -TPO) after their treatment in a formic acid atmosphere. The flow rate of formic acid during the treatment was fixed at 50 mL min^{-1} [STP]. Approximately 0.2 g of NiO–YSZ particles were placed in the center of quartz tube reactor (ID: 8 mm) and first reduced with H_2 for 1 h and then treated at 500, 600, 700 or 800°C under a stream of nitrogen-diluted formic acid vapor for 10 h. After the treatment, the samples were rapidly cooled to room temperature under a nitrogen atmosphere. Approximately 0.05 g of the particles from each treatment were placed into a U-type quartz reactor (ID: 4 mm) for progressive oxidization with O_2 , which was added at a fixed flow rate of 15 mL min^{-1} [STP]. The samples were first purged with O_2 at room temperature for 30 min and then heated to 800°C at $10^\circ\text{C min}^{-1}$. The solid carbon deposited on the Ni–YSZ surface was then gradually oxidized to CO_2 . The effluent gas from the reactor was connected to a Hitachi QIC-20 mass spectroscope (MS) for the in situ monitoring of CO_2 formation. The morphologies of the fresh cells and the cells after formic acid treatment were examined with an environmental scanning electron microscope (SEM, FEI, Quanta-200).

3. Results and discussion

When applying carbon-containing chemicals such as hydrocarbons and oxygenated hydrocarbons as fuels for SOFCs with conventional nickel-based cermet anodes, coke formation is a serious problem because nickel cermet anodes catalyze the pyrolysis of such carbon-containing fuels. The solid carbon formed will occupy the active sites of the nickel surface, thus deteriorating the performance of the anode for fuel oxidation; this accumulation of carbon on the anode may ultimately destroy a fuel cell. Several strategies have been applied to improve the coking resistance of SOFCs operating on hydrocarbons or oxygenated hydrocarbons such as alloying nickel with other less active metals such as iron

and copper [23,24], the development of perovskite-type oxide anodes such as $\text{La}_{1-x}\text{Sr}_x\text{Cr}_y\text{Mn}_{1-y}\text{O}_3$ [25,26], the application of CeO_2 as an electrode catalyst instead of nickel and the development of new anode materials such as Cu-CeO_2 [27,28], and the modification of conventional anodes with a functional layer with improved coking resistance [29,30]. However, in principle, all the above methodologies only alter the reaction kinetics of the oxidation/decomposition reactions of the hydrocarbons and oxygenated hydrocarbons on the electrode; they cannot alter the thermodynamic reaction equilibrium.

This thermodynamic consideration suggests that coke formation remains a practical problem given sufficient operating time. For practical applications, most fuel cells must be capable of operating for tens of thousands of hours. For such a long operating period, coke formation remains a major concern. Thus, the best choice would be to suppress coke formation thermodynamically. It is well known that the formation of carbon is closely related to the oxygen-to-carbon ratio in the fuel gas. To avoid coke formation, a high concentration of steam is introduced when methane is applied as the fuel to allow the internal steam reforming of methane [31,32]. However, the use of water vapor makes the system more complex and less attractive for practical applications.

Because the oxygen-to-carbon ratio in the formic acid molecule is higher than those in methanol and methane, a lower coke formation capacity is expected when applying formic acid as a fuel. The thermodynamic equilibrium compositions in the thermal decomposition of formic acid were first analyzed using the commercial thermodynamics software HSC. To accurately simulate the feed gas used in the experiments, the nitrogen carrier gas was also included during the thermodynamic calculations, and the initial ratio of nitrogen to formic acid was set at 1:1. As shown in Fig. 1, the main decomposition products of formic acid are H_2 , CO_2 , H_2O and CO . This product set suggests that the decomposition of formic acid likely proceeds via two reaction routes: $\text{HCOOH} = \text{H}_2 + \text{CO}_2$ and $\text{HCOOH} = \text{H}_2\text{O} + \text{CO}$. At temperatures lower than 600°C , solid carbon is also a preferred product, whereas carbon formation becomes unfavorable at temperatures higher than 600°C . This thermodynamic product distribution suggests that an operating temperature higher than 600°C can effectively suppress coke formation on the anode when using formic acid as a fuel. In addition, as listed in Table 1, the thermal effects of the two formic acid decomposition reactions above are not obvious, which implies that no additional pre-decomposition step is required when formic acid is used as a fuel.

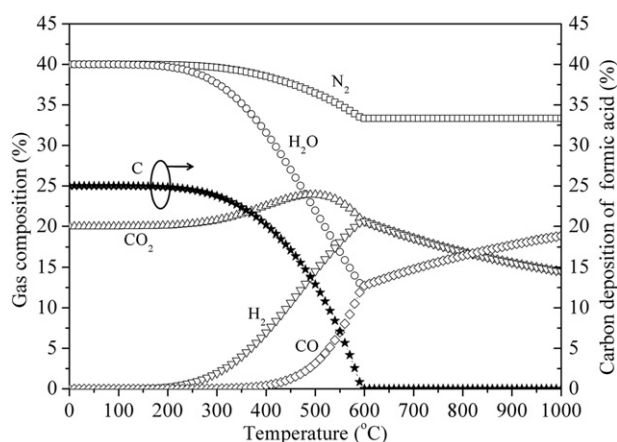


Fig. 1. Temperature dependence of the thermodynamic equilibrium of formic acid decomposition.

Table 1

Standard molar reaction enthalpies of formic acid decomposition reactions.

Reaction	600 °C	650 °C	700 °C	750 °C	800 °C
$\Delta H \text{ (kJ mol}^{-1}\text{)}$ $\text{HCOOH} = \text{H}_2 + \text{CO}_2$	−10.5	−10.5	−10.7	−10.9	−11.1
$\text{HCOOH} = \text{H}_2\text{O} + \text{CO}$	25.8	25.2	24.5	23.8	23

For an experimental demonstration of the potential of formic acid as a fuel for SOFCs with conventional nickel cermet anodes without the problem of coke formation, we first examined the carbon deposition properties of an Ni + YSZ anode in particle form by treating the anode particles in diluted formic acid vapor (using N_2 and HCOOH in a 1:1 molar ratio) at 500, 600, 700 or 800°C for 10 h and then analyzing the material by O_2 -TPO. For comparison, we also examined the carbon deposition properties of an Ni + YSZ cermet anode in methane atmosphere. For this analysis, the treatment was conducted under a methane atmosphere at 650°C for 30 min. As shown in Fig. 2, a large CO_2 peak appeared in the O_2 -TPO profile for the sample treated in a methane atmosphere at 650°C even for only 30 min, whereas only a very small CO_2 peak intensity was observed for the samples after treatment in diluted formic acid at 500°C , and the CO_2 peaks were negligible when the treatment temperature was 600°C or higher. These profiles show that the Ni + YSZ cermet anode did not promote the decomposition of formic acid to form solid carbon, particularly at temperatures higher than 600°C , agreeing fairly well with the thermodynamic calculations. These results further suggest that formic acid may be directly applied as a fuel for SOFCs with conventional nickel cermet anodes without modification. This scheme is highly attractive because it allows for direct application in state-of-the-art SOFCs.

It is well known that carbon deposition on the anode of a fuel cell can create large internal stress within the anode, which can impair the geometric integrity of the fuel cell and even lead to the failure of the fuel cell when sufficient carbon is deposited. For example, we previously reported that the geometric integrity of cells with nickel cermet anodes was seriously impaired after treatment in methane gas [33]. To experimentally determine the mechanical stability of SOFCs with conventional nickel cermet anodes operating directly on formic acid, four half-cells were fabricated with Ni + YSZ anodes supported on thin-film YSZ electrolytes, and three of these cells were then individually treated at 600, 700 or 800°C with nitrogen-diluted formic acid vapor (N_2 and HCOOH in a molar ratio of 1:1) for a period of 10 h. Digital photographs of the fresh cell and the three cells after formic acid treatment are shown in Fig. 3. All three half-cells retained their original

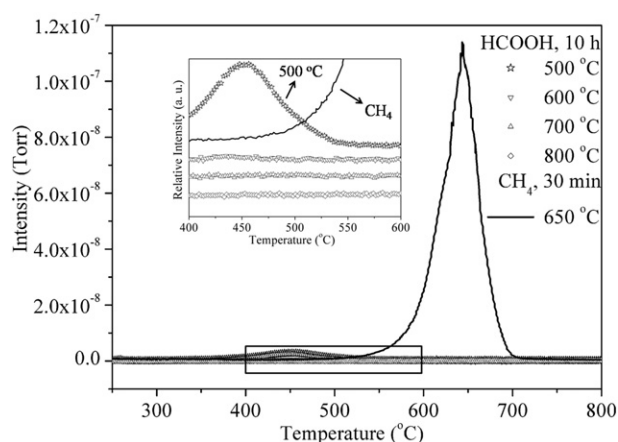


Fig. 2. O_2 -TPO profiles for Ni-YSZ anode particles after treatment in diluted formic acid for 10 h at various temperatures and in methane for 30 min at 650°C .

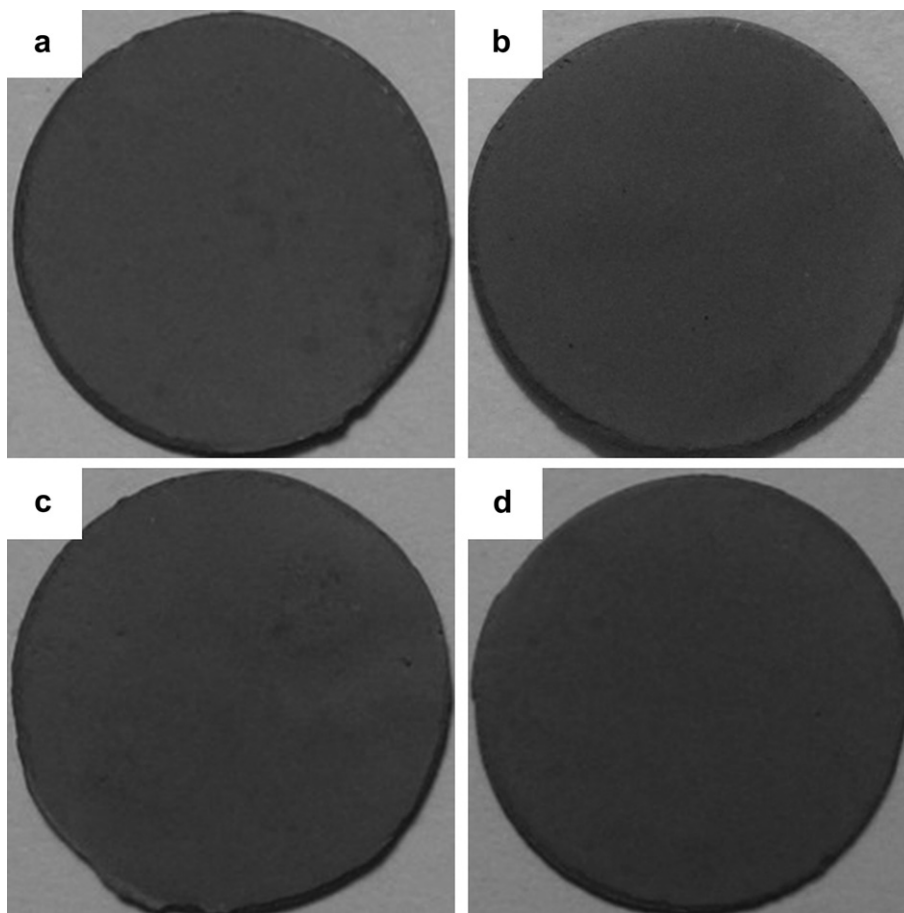


Fig. 3. Digital photographs of anode surfaces of four different half-cells: (a) a fresh half-cell; (b) a half-cell after 10 h of treatment in formic acid at 600 °C; (c) a half-cell after 10 h of treatment in formic acid at 700 °C; (d) a half-cell after 10 h of treatment in formic acid at 800 °C.

morphology without visible carbon deposition after the treatment, as expected. The absence of carbon deposition was also supported by the small changes in the masses of the three cells after formic acid treatment, as listed in Table 2. According to our preliminary analysis, the degree of possible coke formation should be most obvious on the half-cell treated at 600 °C compared with other cells treated at 700 and 800 °C, so we further examined the microstructural changes of the anode treated in formic acid at 600 °C by SEM. Fig. 4a and b presents SEM images of a fresh Ni–YSZ anode, and Fig. 4c and d shows the Ni–YSZ anode after treatment in formic acid at 600 °C for 10 h. No obvious microstructural changes were observed. In addition, by comparing with the distinct carbon deposition of methane over Ni–YSZ anode under similar condition studied by Hongpeng He et al. [34], there should be no deposited carbon on either the surface or the cross-section of the Ni–YSZ anode after the formic acid treatment.

Considering the intriguing coke-free nature of formic acid oxidation over the Ni–YSZ anode at intermediate temperatures (600–800 °C), we investigated the performance of this fuel in a working cell by directly applying nitrogen-diluted formic acid at

a concentration of approximately 50% as a fuel in an anode-supported SOFC. The flow rate of N₂ gas was held constant at 150 mL min^{−1} [STP]. For comparison, we also tested a fuel cell with pure hydrogen or 25% H₂ in N₂ as fuels. As shown in Fig. 5a, peak power densities of 888, 630, 523, 268, and 159 mW cm^{−2} were achieved at 800, 750, 700, 650 and 600 °C, respectively, by applying pure hydrogen as the fuel. The *I*–*V* polarization curves are straight even at high temperatures, suggesting that the electrode reactions on the anode are rapid and experience negligible concentration polarization. By applying diluted hydrogen (75 mL min^{−1} H₂ + 225 mL min^{−1} N₂) as the anode gas, as shown in Fig. 5b, the peak power densities reached 683, 527, 360, 216 and 120 mW cm^{−2} at 800, 750, 700, 650 and 600 °C, respectively, slightly lower values than those achieved by applying pure hydrogen as the fuel. In addition, obvious concentration polarization was observed at high current density and high temperatures. This result indicates that nitrogen not only introduced a diluting effect on the hydrogen to cause the slight decrease in power output but also reduced the hydrogen diffusion rate. An improvement of the anode porosity is then required to reduce such concentration polarization.

Fig. 5c presents the *I*–*V* and *I*–*P* polarization curves of a similar cell operating on 150 mL min^{−1} formic acid + 150 mL min^{−1} N₂ [STP]. Peak power densities of 571, 501, 372, 238 and 128 mW cm^{−2} were achieved at 800, 750, 700, 650 and 600 °C, respectively. Similar concentration polarization was also observed at elevated temperatures. Comparing these results with those using diluted hydrogen as the fuel, the power outputs at 800 and 750 °C for the cell operating on diluted formic acid as a fuel was slightly lower.

Table 2

Masses of three half-cells before and after the treatment in formic acid vapor.

		600 °C	700 °C	800 °C
Masses of half-cells (g)	Before test	0.309(2)	0.387(4)	0.316(0)
	After test	0.309(1)	0.387(5)	0.316(4)

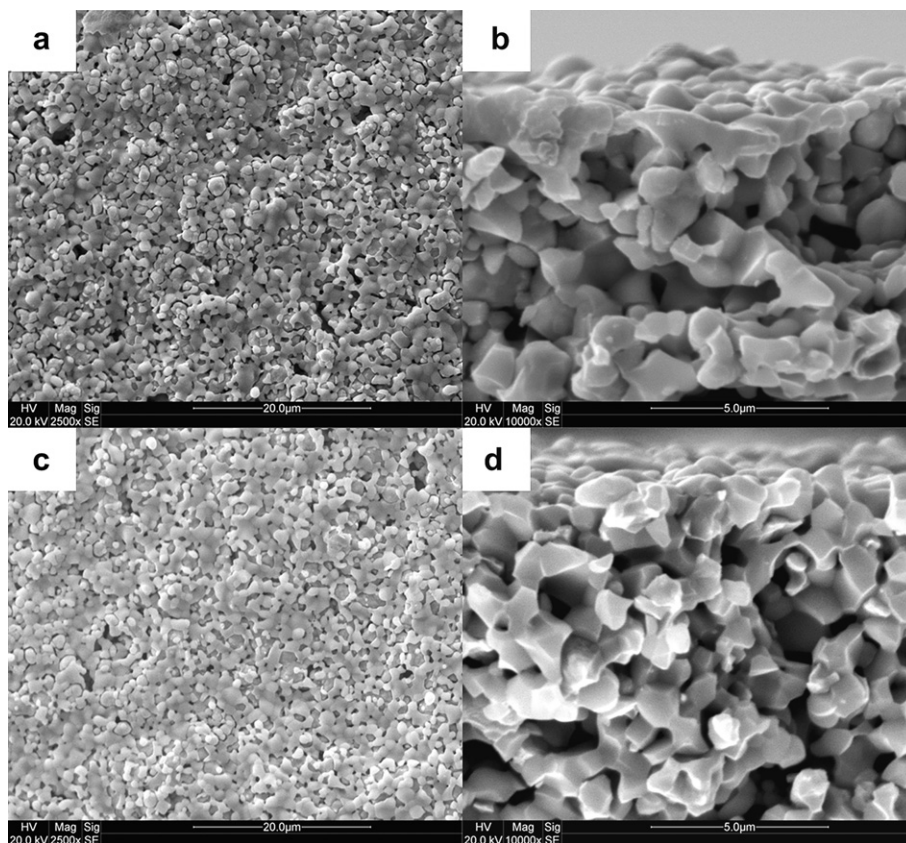


Fig. 4. SEM images of (a) the surface and (b) the cross-section of a fresh Ni–YSZ anode; (c) the surface and (d) the cross-section of a Ni–YSZ anode after 10 h of treatment in formic acid at 600 °C.

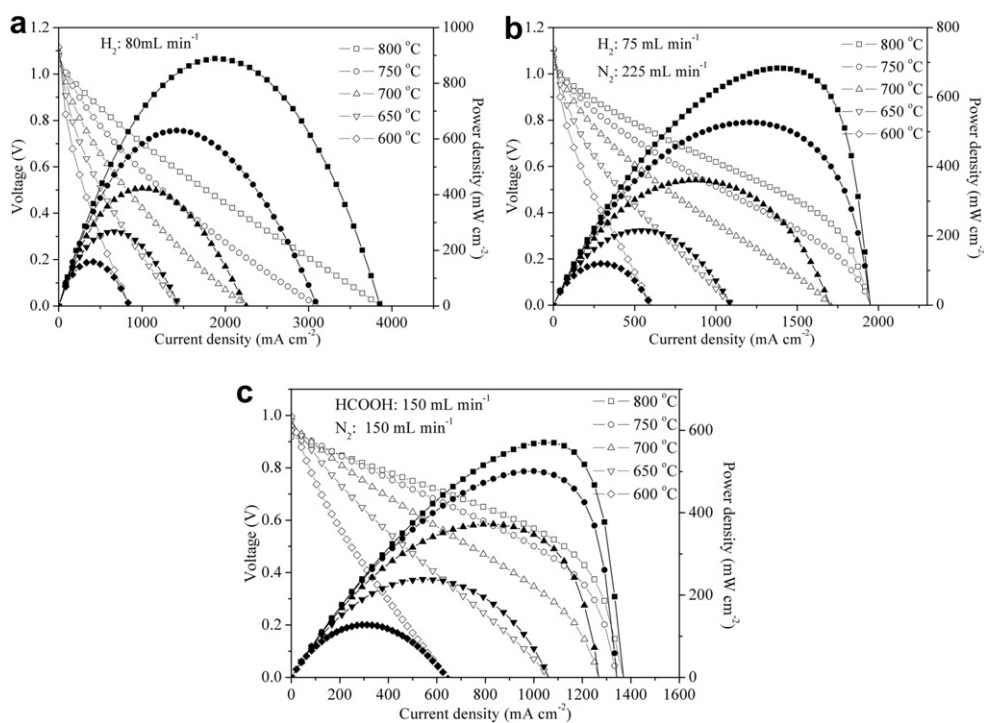


Fig. 5. The *I*–*V* and *I*–*P* curves of single cells operating on (a) pure H₂, (b) diluted H₂, and (c) diluted formic acid.

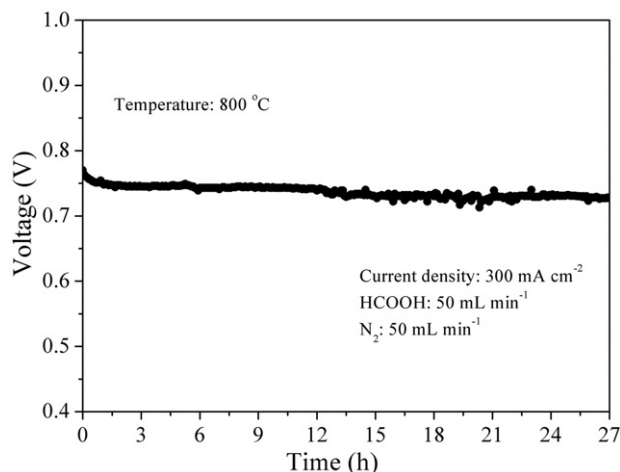


Fig. 6. The voltage-versus-time curve of a single cell operating on formic acid at 800 °C with a constant current density of 300 mA cm⁻².

However, at lower temperatures, the difference in power output with the use of the two fuels became much less significant. It is well known that CO has a lower electrochemical oxidation rate than H₂ over nickel cermet anodes. As demonstrated here, formic acid decomposition can proceed by two different routes: $\text{HCOOH} = \text{H}_2 + \text{CO}_2$ or $\text{HCOOH} = \text{H}_2\text{O} + \text{CO}$. According to the results of our theoretical thermodynamic calculations for formic acid decomposition shown in Fig. 1, the proportion of H₂ increases as temperature is decreased. This observation well explains the lower power outputs of the cell using diluted formic acid as a fuel than that with diluted hydrogen as a fuel at high temperatures (750 and 800 °C), but this difference was less significant at lower temperatures (600, 650 and 700 °C).

As described above, coking is a major concern for SOFCs operating on carbon-containing fuels. Previously, based on the thermodynamic calculation, it was demonstrated that the coke formation was thermodynamically unfavorable at temperature higher than 600 °C. To further demonstrate the feasibility of direct feeding SOFC with formic acid, a cell was operated with diluted formic acid at 800 °C for a period of ~30 h; during the measurement, mesh-like silver was applied as the current collector [35]. Fig. 6 illustrates the time dependence of cell voltage at a constant current density of 300 mA cm⁻². The cell voltage remained at a value of approximately 0.74 V, although a slight fluctuation was observed. After the stability test, the cell still maintained good geometric integrity without the formation of cracks. This test result further supports the assertion that the formic acid can be directly applied to an SOFC with a state-of-the-art anode without the problem of coke formation.

4. Conclusions

In this study, pure formic acid was directly applied as fuel for SOFCs. The results of theoretical thermodynamic calculations suggested that carbon formation was unfavorable in the thermal decomposition of formic acid at temperatures above 600 °C. The experimental results also evidenced that carbon deposition was not a practical problem on a conventional Ni–YSZ anode with formic acid as a fuel. The high oxygen-to-carbon ratio of formic acid disfavors carbon deposition on a Ni–YSZ anode. An SOFC run with

formic acid as a fuel showed a promising power output of 571 mW cm⁻² at 800 °C, much higher than that of direct formic acid in a PEMFC, with a reported value of approximately 100 mW cm⁻². Because of its coke-free nature, long-term stable cell performance was also obtained. Together, the results of this study suggest that formic acid has great promise as a direct fuel for SOFCs with conventional nickel cermet anodes. Due to the high volumetric energy density, easy transportation, and wide availability of formic acid, such fuel cells may find applications as power sources for portable devices and vehicles.

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References

- [1] D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, *Chem. Soc. Rev.* 37 (2008) 1568–1578.
- [2] H.W. Zhang, P.K. Shen, *Chem. Soc. Rev.* 41 (2012) 2382–2394.
- [3] A. Kirubakaran, S. Jain, R.K. Nema, *Renew. Sustain. Energy Rev.* 13 (2009) 2430–2440.
- [4] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, *J. Power Sources* 117 (2003) 22–25.
- [5] R. Dillon, S. Srinivasan, A.S. Aricò, V. Antonucci, *J. Power Sources* 127 (2004) 112–126.
- [6] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, *J. Power Sources* 163 (2007) 743–754.
- [7] C. D’Urso, V. Baglio, V. Antonucci, A.S. Aricò, S. Specchia, U.A. Icardi, G. Saracco, C. Spinella, G. D’Arrigo, *Int. J. Hydrogen Energy* 36 (2011) 8088–8093.
- [8] M.A. Medinsky, D.C. Dorman, *Toxicol. Lett.* 82/83 (1995) 707–711.
- [9] A. Heinzel, V.M. Baragan, *J. Power Sources* 84 (1999) 70–74.
- [10] T. Seiler, E.R. Savinova, K.A. Friedrich, U. Stimming, *Electrochim. Acta* 49 (2004) 3927–3936.
- [11] A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* 1 (2008) 751–758.
- [12] C. Rice, S. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *J. Power Sources* 111 (2002) 83–89.
- [13] C.M. Miesse, W.S. Jung, K.J. Jeong, J.K. Lee, J. Lee, J. Han, S.P. Yoon, S.W. Nam, T.H. Lim, S.A. Hong, *J. Power Sources* 162 (2006) 532–540.
- [14] P. Hong, F. Luo, S.J. Liao, J.H. Zeng, *Int. J. Hydrogen Energy* 36 (2011) 8518–8524.
- [15] K. Eguchi, H. Kojo, T. Takeguchi, R. Kikuchi, K. Sasaki, *Solid State Ionics* 152–153 (2002) 411–416.
- [16] S. McIntosh, R.J. Gorte, *Chem. Rev.* 104 (2004) 4845–4865.
- [17] Y.F. Yi, A.D. Rao, J. Brouwer, G.S. Samuelsen, *J. Power Sources* 144 (2005) 67–76.
- [18] C. Su, W. Wang, R. Ran, T. Zheng, Z.P. Shao, *Int. J. Hydrogen Energy* 37 (2012) 6844–6852.
- [19] B.C.H. Steele, *Nature* 400 (1999) 619–621.
- [20] T. Chen, W.G. Wang, H. Miao, T.S. Li, C. Xu, *J. Power Sources* 196 (2011) 2461–2468.
- [21] C. Su, R. Ran, W. Wang, Z.P. Shao, *J. Power Sources* 196 (2011) 1967–1974.
- [22] B.C. Eigenbrodt, M.B. Pomfret, D.A. Steinhurst, J.C. Owrutsky, R.A. Walker, *J. Phys. Chem. C* 115 (2011) 2895–2903.
- [23] B. Huang, S.R. Wang, R.Z. Liu, T.L. Wen, *J. Power Sources* 167 (2007) 288–294.
- [24] H. Kim, C. Lu, W.L. Worrell, J.M. Vohs, R.J. Gorte, *J. Electrochem. Soc.* 149 (2002) A247–A250.
- [25] S.W. Tao, J.T.S. Irvine, *Nat. Mater.* 2 (2003) 320–323.
- [26] S.W. Tao, J.T.S. Irvine, J.A. Kilner, *Adv. Mater.* 17 (2005) 1734–1737.
- [27] R.J. Gorte, S. Park, J.M. Vohs, C.H. Wang, *Adv. Mater.* 12 (2000) 1465–1469.
- [28] O.C. Nunes, R.J. Gorte, J.M. Vohs, *J. Power Sources* 141 (2005) 241–249.
- [29] Z.L. Zhan, S.A. Barnett, *Science* 308 (2005) 844–847.
- [30] W. Wang, W. Zhou, R. Ran, R. Cai, Z.P. Shao, *Electrochem. Commun.* 11 (2009) 194–197.
- [31] J. Meusinger, E. Riensche, U. Stimming, *J. Power Sources* 71 (1998) 315–320.
- [32] N. Laosiripojana, S. Assabumrungrat, *Appl. Catal. A: Gen* 290 (2005) 200–211.
- [33] W. Wang, C. Su, Y.Z. Wu, R. Ran, Z.P. Shao, *J. Power Sources* 195 (2010) 402–411.
- [34] H.P. He, J.M. Hill, *Appl. Catal. A: Gen* 317 (2007) 284–292.
- [35] Y.B. Chen, F.C. Wang, D.J. Chen, F.F. Dong, H.J. Park, C. Kwak, Z.P. Shao, *J. Power Sources* 210 (2012) 146–153.